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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title: UV CURABLE GEL COATS</b> <b>(54) Titre: ENDUITS GELIFIES DURCISSABLES AUX UV</b>  <b>(57) Abstract</b> <p>A gel coat composition comprises a resinous or oligomeric component containing (meth)acrylate functionality, a (meth)acrylate ester, and a polymerization initiator that can be activated under ultraviolet light. In one embodiment, the polymerization initiator is a non-peroxide initiator and the gel coat composition is devoid of aryl vinyl monomer.</p> <b>(57) Abrégé</b> <p>Une composition d'enduit gélifié comprend un composé résineux ou oligomérique qui possède une fonction (meth)acrylate et qui renferme un (meth)acrylate ester ainsi qu'un initiateur de polymérisation pouvant être activé par rayonnement ultraviolet. Selon un mode de réalisation, l'initiateur de polymérisation est un initiateur non peroxyde et la composition pour enduit gélifié ne renferme pas de monomère aryle vinylique.</p>		

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<b>(21) International Application Number:</b> PCT/US99/22596 <b>(22) International Filing Date:</b> 29 September 1999 (29.09.99)  <b>(30) Priority Data:</b> 60/102,452 30 September 1998 (30.09.98) US  <b>(71) Applicant (for all designated States except US):</b> REICHHOLD, INC. [US/US]; 2400 Ellis Road, Durham, NC 27703 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ADAMS, Robert, Mark [US/US]; 103 Hillside Court, Cary, NC 27511 (US). CREMASCHI, Jorge, A. [US/US]; 101 Appomattox Road, Cary, NC 27513 (US). PHAN, Xuan, Thanh [US/US]; 2509 Sunnystone Way, Raleigh, NC 27613 (US). RIGGS, Gary, A. [US/US]; 1008 Barrasesett Court, Wake Forest, NC 27587 (US).  <b>(74) Agents:</b> SMITH, Robert, J. et al.; Myers, Bigel, Sibley, & Sajovec, P.A., P.O. Box 37428, Raleigh, NC 27627 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> UV CURABLE GEL COATS  <b>(57) Abstract</b>  A gel coat composition comprises a resinous or oligomeric component containing (meth)acrylate functionality, a (meth)acrylate ester, and a polymerization initiator that can be activated under ultraviolet light. In one embodiment, the polymerization initiator is a non-peroxide initiator and the gel coat composition is devoid of aryl vinyl monomer.			

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## UV CURABLE GEL COATS

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### Cross-Reference to Related Applications

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The instant application claims priority to U.S. Provisional Patent Application Serial No. 60/102,452 filed 30 September 1998, the disclosure of which is incorporated herein by reference in its entirety.

### Field and Background of the Invention

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The present invention relates to a gel coating composition, and its use on the surface of a synthetic article to provide surface hardness, impact resistance, abrasion resistance, heat resistance, resistance to stains, burns and the like.

35

Gel coats are typically applied to the surface of a mold to produce a layer or layers on which a composite article will be produced. Usually, the surface of the resulting gel coat where it contacts air is then lined with either a composition made of an unsaturated polyester resin and glass fibers so as to produce a shaped fiber-reinforced plastic article (e.g., a boat hull), or with a composition made of an unsaturated polyester resin and a filler to make a shaped plastic article such as simulated marble, (e.g. dressing tables, kitchen counters, bathtub enclosures and the like).

40

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Of particular interest are gel coats used in preparing so-called "cultured stone" articles including, for example, "cultured marble", "cultured onyx" and "cultured granite". Cultured stone is formed by first creating a mold of a desired shape, and spraying the mold surface with a conventional gel coat. Pigments may or may not be added to the gel coat to give it the desired color

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5 or pattern. After the gel coat hardens, a catalyzed mixture of an unsaturated polyester resin and a desirable filler is poured onto this layer and allowed to solidify. The article is removed from the mold with the gel coat layer now forming the outer surface of the finished product. Examples of suitable gel coating resins may be found in U.S. Pat. No. 4,543,366 to Smith, U.S. Pat. No. 5,028,459 to Lathrop and U.S. Pat. No. 4,664,982 to Genovese, et al., the disclosures of each of which are herein incorporated by reference in their entirety.

10 Conventional gel coats, however, often utilize peroxides to initiate curing. Such peroxides are regarded as hazardous because of their combustibility and skin contact issues, and there are environmental concerns with respect to ground water exposure. Additionally, the use of peroxides requires a minimum casting time of about one hour, which is a limiting step in the manufacturing process.

15 Many conventional gel coats release high levels of VOC such as styrene during processing. Various VOCs including styrene monomer are believed to be potentially harmful to both the environment and people and are often heavily regulated with a reduction in the amount thereof to zero being very desirable.

20 To this end, there is a need in the art to provide a gel coat composition and a method of applying a gel coat composition to a surface of a synthetic molded article (e.g. cultured marble) that eliminates the need for peroxides to cure the gel coat resin and obviates the time constraints of the use of peroxides; while also substantially eliminating VOCs by eliminating volatile solvents or volatile reactants such as aryl vinyl monomers like styrene. This is accomplished by using a UV (ultraviolet) curable composition that is peroxide-free and solvent-free (e.g., free of aryl vinyl monomer). Particularly preferred compositions contain a UV curable urethane (meth)acrylate and/or epoxy (meth)acrylate.

### 30 Summary of the Invention

In one aspect, the invention relates to a gel coat composition. The gel coat composition comprises a resinous or oligomeric component containing (meth)acrylate functionality, a (meth)acrylate ester, and a

polymerization initiator that can be activated under ultraviolet light, the polymerization initiator being a non-peroxide initiator. The gel coat composition is advantageously devoid of aryl vinyl monomer. Preferably, a performance additive may also be employed in the gel coat composition.

In another aspect, the invention relates to an article of manufacture. The article of manufacture comprises a substrate having a surface and a gel coat composition present on the surface of the substrate. The gel coat composition comprises a resinous or oligomeric component containing (meth)acrylate functionality, a (meth)acrylate ester, and a polymerization initiator that can be activated under ultraviolet light. The polymerization initiator is a non-peroxide initiator and the gel coat composition is devoid of aryl vinyl monomer. In a preferred embodiment, a performance additive may also be employed in the gel coat composition.

In another aspect, the invention relates to a method of forming an article of manufacture. The method comprises applying a gel coat composition to a surface of a mold, the gel coat composition comprising a component containing (meth)acrylate functionality, a (meth)acrylate ester, and a polymerization initiator that can be activated under ultraviolet light. Preferably, a performance additive may also be employed in the gel coat composition. The gel coat composition is cured and lined with a substrate to form an assembly. The assembly is de-molded to form an article of manufacture.

The invention will now be described in greater detail with reference to its preferred embodiments.

#### Detailed Description of the Preferred Embodiments

The invention will now be described in greater detail to its preferred embodiments. It should be appreciated however that these embodiments serve merely to illustrate the invention, and do not limit the scope of the invention as defined by the claims.

Any number of components having (meth)acrylate functionality can be employed in the gel coat composition of the invention. Exemplary resins or oligomers having (meth)acrylate functionality may be employed and include, but are not limited to, urethane (meth)acrylates and epoxy (meth)acrylates.



For the purposes of the invention, an oligomer may be a reaction product in which the chemical units may occur more than once.

With respect to urethane (meth)acrylates, such compounds are typically obtained by reacting an isocyanate, a polyol and a hydroxyalkyl acrylate. Examples of the isocyanates include, but are not limited to, 2,4-tolylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, xylene diisocyanate, hydrogenated xylene diisocyanate, dicyclohexylmethane diisocyanate, tolidine diisocyanate, naphthalene diisocyanate, triphenylmethane triisocyanate, trimethylol propane TDI adducts sold under the tradename Burnock D-750, CRISVON NX (produced by Dainippon Ink & Chemicals, Inc.), DESMODUR DL (produced by Sumitomo-Bayer Co., Ltd.), CORONATE L (produced by Nihon Polyurethane Co., Ltd.), Takenate D102 (produced by Takeda Pharmaceutical Co.), Isonate 143L (produced by Mitsubishi Chemical Industries, Ltd.), and the like. These compounds may be used alone or in combinations of two or more. Among the aforementioned diisocyanates, use of isophorone diisocyanate is particularly preferred.

Suitable polyols typically have at least two hydroxyl groups. Such polyols are known ones which are generally used in production of polyurethane resins, and include, for example, low molecular weight glycols, low molecular weight polyols, polyether polyols, polyester polyols, polybutadiene polyols, hydrogenated polybutadiene polyols, silicon-containing polyols, and phosphorus-containing polyols. As low molecular weight glycols, for example, usable are ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, 1,3-butanediol, 1,4-butanediol, pentaethylene glycol, hexamethylene glycol, neopentyl glycol, 2-ethyl-1,3-hexanediol, and bisphenol A. As low molecular weight polyols, for example, usable are trimethylolpropane, glycerin pentaerythritol, erythritol, and sorbitol. As polyether polyols, for example, usable are polymers or copolymers of ethylene oxide, propylene oxide or tetrahydrofuran.

Suitable hydroxy alkyl acrylates include 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxycyclohexyl acrylate, caprolactone-modified

5 hydroxethyl acrylate, 5-hydroxycyclooctyl acrylate, 2-hydroxy-3-phenyloxy-propyl acrylate, and pentaerythritol triacrylate.

Any number of epoxy (meth)acrylates may be used in the gel coat composition of the invention. An example of an epoxy (meth)acrylate includes  
10 5 one that is selected from resins having terminal (meth)acrylic groups, which are usually obtained by modifying various epoxy resins such as bisphenol A type epoxy resins, bisphenol F type epoxy resins, polyphenol type epoxy resins, halogenated bisphenol type epoxy resins, polyhydric glycidyl ester  
15 type epoxy resins, glycidyl ether type resins, and peracetate oxidized type epoxy resins. The terminal (meth)acrylic groups are polymerized and crosslinked utilizing conventional techniques such as ultraviolet cure  
20 technology.

Polymerization catalysts also may be used such as dibutyl tin dilaurate, zinc octoate, dioctyl tin carboxylate, and dibutyl tin di-2-ethylhexoate.

15 25 The resinous or oligomeric component containing (meth)acrylate functionality can be used in various amounts. Preferably, the gel coat composition comprises from about 5 to about 95 percent by weight of the resinous or oligomeric component, and more preferably from about 15 to  
30 about 55 percent by weight.

20 A (meth)acrylate ester may be employed in the composition in various amounts and may function as a reactive diluting agent. Examples of (meth)acrylate esters include, but are not limited to,  
35 tetrahydrofurfuryl(meth)acrylate, 2-ethylhexyl(meth)acrylate, methoxyethyl (meth)acrylate, N-vinylpyrrolidone, phenyl(meth)acrylate, 2-hydroxyethyl  
25 (meth)acrylate, diethyleneglycol di(meth)acrylate, tetraoxyethyleneglycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, dipentaerythritol  
40 hexa(meth)acrylate, trimethylolpropane di(meth)acrylate, tripropyleneglycol di(meth)acrylate, isobornyl (meth)acrylate, and pentaerythritol  
tetra(meth)acrylate. Mixtures of any of the above. For example, the  
45 30 (meth)acrylate ester may be used in an amount ranging from about 5 to about 95 percent based on the weight of the gel coat composition, and more preferably from above 0 to about 50 percent based on the weight of the gel  
50 coat composition.

5 The gel coat compositions of the present invention may further incorporate performance additives, as required, such as, but not limited to, organic or inorganic thixotropes, organic or inorganic pigments, stabilizers, defoaming agents, wetting agents, and leveling agents. Suitable organic and  
10 5 inorganic thixotropes include, for example, silica powders, asbestos powders, hydrogenated castor oil, aliphatic acid amides, and other known thixotropes. Mixtures of any of the above may also be used.

15 As the photoinitiator that can be used for the polymerization under ultraviolet light, there can be mentioned carbonyl compounds such as  
10 acetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxyacetophenone, 4'-isopropyl-2-hydroxy-2-methylpropiophenone, 2-hydroxy-2-methylpropiophenone, 4,4'-bis-(diethylamino)benzophenone, benzophenone, methyl-(o-benzoyl) benzoate, 1-phenyl-1,2-propanedione-2-(o-ethoxycarbonyl)oxime, 1-phenyl-1,2-propanedione-2-(o-benzoyl)oxime,  
20 benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin isooctyl ether, benzil, benzil diethyl ketal and diacetyl, benzyldimethyl ketal, mono and bis acyl phosphine oxides, anthraquinone; and xanthone compounds such as methylantraquinone, chloroanthraquinone, 2-methylthioxanthone and 2-isopropylthioxanthone; and  
30 sulfur compounds such as diphenyl sulfide and dithiocarbamate. A particularly preferred compound is Irgacure 184, which is a hydroxycyclohexylphenyl ketone. The gel coat composition preferably  
35 comprises from above 0 to about 10 percent by weight of the polymerization initiator, more preferably from above 0 to about 2 percent by weight.

25 As described herein, an article of manufacture comprises a substrate with a gel coat composition present on the surface of the substrate, preferably coated thereon. Any number of substrates that employ gel coats may be employed and include, but are not limited to, a fiber-reinforced plastic based on thermosetting resins, cultured stone which includes, but is not limited to,  
40 30 cultured marble, cultured onyx, cultured granite, and combinations thereof. Natural or simulated marble may be employed. Examples of fibrous materials that can be employed, as well as examples of thermosetting resins are set forth in greater detail hereinbelow.

5 The gel coat composition of the present invention is applied with a suitable method such as spraying or brushing to the surface of a mold in a desired shape to give a uniform film thickness that usually ranges from about 0.01 to about 0.7 mm (about 8 to about 10 mils). This film is then  
10 subsequently cured with typically ultraviolet radiation. Coating operations are usually performed at ambient temperature, with the mold being typically held at ambient temperature or in the range of about 40° to about 150° C. The applied gel coat composition may be cured at ambient temperature, typically in the range of about 20° C to about 80° C.

15 After curing, the gel coat, while still on the mold, is preferably lined with a layer of a fiber-reinforced plastic based on thermosetting resins or cultured stone as described herein, and the assembly is cured and de-molded to form a shaped article having the gel coat as a surface layer.

20 Suitable thermosetting resins are selected from the group consisting of  
25 an unsaturated polyester resin, a vinyl ester resin, an epoxy resin, an acrylic resin and a urethane resin and which can be shaped in a desired form under properly selected conditions such as at ambient temperature, under heating, at atmospheric pressure or a superatmospheric pressure; and a fibrous reinforcement and/or an inorganic or organic filler, such as described in U.S.  
30 Patent No. 4,916,023 to Kawabata, et al. the disclosure of which is incorporated herein by reference in its entirety. Other examples of fillers include, but are not limited to, fiberglass, carbon fiber, naturally occurring fibrous compound, calcium carbonate, aluminum trihydrate, talc, ground silicates, silica spheres, polymeric spheres, pigmented particulates, and  
35 combinations thereof. These fillers may be used in making cultured stone articles.

## EXAMPLES

### Example 1

40 A polyester urethane acrylate, Uretuf™ 4210 available from Reichhold, Inc., Research Triangle Park, North Carolina is blended to provided a UV curable gel coat as follows:

5	<b><u>Component</u></b>	<b><u>Weight %</u></b>
	Polyester urethane acrylate (Uretuf™ 4210)	40.0
	Trimethylolpropane triacrylate	15.0
5	Tripropyleneglycol diacrylate	44.5
10	Irgacure 184	0.5
	Aerosil 200	1.0

**Example 2**

10 An epoxy acrylate, Epotuf™ 3230 25TPGDA available from Reichhold,  
 15 Inc., Research Triangle Park, North Carolina is blended the same as in  
 Example 1 to provide a UV curable epoxy acrylate with the epoxy being a  
 75/25 blend of the Epotuf™ 3230 and tripropyleneglycol diacrylate and being  
 20 present at an amount of 40 weight percent.

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**Example 3****UV Light Resistance Study**

25 Experimental gel coat formulations are drawn down over 12" x 12" x ¼"  
 pre-waxed glass plates to cured thicknesses as noted below. A marble matrix  
 20 is prepared by mixing together the following: 650g of Polylite™ 32145-08  
 made available from Reichhold, Inc., 39g DuPont R-900™ TiO<sub>2</sub> made  
 30 available from E.I. Dupont de Nemours of Wilmington, Delaware, and 1950g  
 ECC Marblemite™ (CaCO<sub>3</sub>) made available from ECC of Sylacauga,  
 Alabama. The mixture is blended together, and 6.5cc of Superox™ 46709  
 35 MEKP is added and mixed for one minute (i.e., until well dispersed). The  
 mixture is immediately poured into a cavity area created by 1" x 1"  
 polypropylene divider bars adhered to the perimeter of the glass plates, filling  
 to approximately 1mm from the top of the bar. The glass panel is manually  
 40 rocked over the edge of a lab bench in order to "vibrate" any air entrapped  
 30 against the film surface to facilitate its release. The resulting matrix is allowed  
 to gel and cure overnight. The entire panel is demolded from the glass plate,  
 and the masking tape and divider bars are removed from the marble casting.

45

Cover ½ of each gel coated surface with aluminum foil. This becomes  
 the "covered" (control reference) area and is typically necessary in order to  
 35 subtract out any changes in color due to heat or humidity alone apart from the  
 50 UV influence. The remaining surface area is designated as the "uncovered"

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surface and is used to determine the affects of UV alone. QUV testing is performed using a Q-panel Accelerated Weathering Tester with A-340 bulbs. The cycle is set to 4 hours of light at 60°C and 4 hours of condensation at 50°C. Total irradiance is set to 1.54 W/m<sup>2</sup>/nm (2 x 0.77). The test period is prepared for 100 total hours (i.e., 50 hours UVA). The color is measured using a Minolta® CR-200 chromameter and reported in Hunter L, a, and b values (described in detail herein). Three readings are taken in a single spot and averaged. Film readings are taken using the calibration tile as the substrate. Panels containing a marble matrix are read directly using the calibration tile as the reference point and reported as an absolute value.

Gel coat composition 3664-51B is employed on marble in tests L through Q listed in Table 1. Tests D through I employ a conventional technology. The gel coat 3664-51B has the following composition:

<u>Ingredient</u>	<u>weight percent</u>
Uretuf™ 4210	42.0
Trimethylolpropane triacrylate	15.0
Tripropyleneglycol diacrylate	39.0
Aerosil™ 200	1.25
Tween™ 20	0.30
Benzophenone	1.00
Darocur™ 1173	3.00

Darocur™ 1173 is made available from Ciba, Inc. of Basel, Switzerland. The following additives are employed in these runs as set forth in Table 1 and are intended to maintain color during exposure to UV energy: T-1130 (a substituted benzotriazole); T-292 (hindered amine); T-400 (hindered amine); and U-3039 (an acrylic ester compound, Uvinul™ by BASF). The letter "T" in the above designation refers to Tinuvin™ from Ciba. The letters "L", "a", and "b" are dimensionless numbers generated by a colorimeter indicating lightness/darkness and color ratios. In particular, these numbers correspond to the Hunter Color Scale which utilizes a 3 axis (x,y,z) system to measure color. It eliminates the subjectivity of measuring color. "L" corresponds to color intensity (light to dark), "a" corresponds to red-green, and "b" corresponds to yellow-blue. The "b" scale specifically measures any changes of yellowness, which is the primary change affected by UV exposure.

5 By indicating the changes in the "b" values, it can be shown how yellow a test specimen becomes after 50 hours of exposure to UV energy in the A spectrum (closest to sunlight). The greater the  $\Delta$  (delta)-b, the more yellow the panel becomes which is not desirable.

10 5 These parameters are evaluated for "covered" and "exposed" samples. "Covered" refers to the sample being shielded from the light, while "exposed" refers to half of the sample being exposed to UV radiation.

15 Table 1 lists the results of the study. In general, the compositions of the invention advantageously display comparable results relative to  
10 conventional technology.

Table 1: QUV versus UV absorbers

	D	E	F	G	H	I	L	M	N	O	P	Q
Type	Mar bl	Mar bl	Mar b	Mar bl	Mar bl	Mar bl	Film	Film	Film	Film	Film	Film
366 4- 51B	N/A	NA	NA	NA	NA	NA	100	100	100	100	100	100
TiO 2	1.5	1.5	1.5	1.5	1.5	1.5	NA	NA	NA	NA	NA	NA
T- 113 0			0.30					0.30				0.15
T- 292				0.30					0.30			
T- 400					0.30					0.30		
U- 303 9						0.30					0.30	0.15
L	94.5 9	92.3 7	94.2 6	94.4 7	94.5 9	94.6 8	96.1 6	96.2 2	95.8 5	95.8 9	95.8 3	94.7 9
a	- 0.70	- 0.69	- 0.83	- 0.83	- 0.80	- 0.88	- 0.82	- 0.83	- 0.90	- 0.86	- 0.93	- 0.97
b	2.40	1.79	3.15	3.00	2.90	3.02	3.89	3.95	4.01	3.89	4.07	4.80
L	94.1 5	92.2 3	93.8 4	93.6 8	94.2 1	94.0 5	96.3 9	96.0 0	95.5 6	95.7 5	95.2 6	94.7 0
a	- 0.55	- 0.56	- 0.53	- 0.49	- 0.59	- 0.60	- 2.14	- 2.02	- 1.94	- 2.05	- 2.62	- 2.84
b	2.83	2.16	3.27	2.92	3.03	3.03	7.87	7.55	7.83	8.02	10.1 4	11.3 9
b	0.43	0.37	0.12	- 0.08	0.13	0.01	3.98	3.60	3.82	4.13	6.07	6.59



Example 4**UV Light Resistance Study**

The procedure according to Example 3 except that the following gel coat compositions were employed:

**1.**

<u>ingredient</u>	<u>parts by weight</u>
Uretuf™ 4200	40
(polyester urethane acrylate)	
Trimethylolpropane triacrylate	15.0
Tripropyleneglycol diacrylate	44.5
Irgacure™ 184	0.5
Aerosil™ 200	1.0

15

Viscosity Data (LV 2)

at 6 rpm	520
at 60 rpm	460

20

Thixotropic Index 1.13

**2.**

<u>ingredient</u>	<u>parts by weight</u>
Uretuf™ 4210	40
Trimethylolpropane triacrylate	15.0
Tripropyleneglycol diacrylate	44.5
Irgacure™ 184	0.5
Aerosil™ 200	1.0

30

Viscosity Data (LV 2)

at 6 rpm	680
at 60 rpm	590

35

Thixotropic Index 1.15

**3.**

<u>ingredient</u>	<u>parts by weight</u>
Epotuf™ 3230 25TPGDA	55
(epoxy acrylate)	

40

5		Trimethylolpropane triacrylate	15.0
		Tripropyleneglycol diacrylate	29.5
		Irgacure™ 184	0.5
		Aerosil™ 200	1.0

5

10		Viscosity Data (LV 2)	
		at 6 rpm	1040
		at 60 rpm	572

15	10	Thixotropic Index	1.82
----	----	-------------------	------

## 4.

20		<u>ingredient</u>	<u>parts by weight</u>
	15	Uretuf™ 4210	40
		Trimethylolpropane triacrylate	20.0
		Isobornyl acrylate	39.5
		Irgacure™ 184	0.5
25		Aerosil™ 200	1.0

20

		Viscosity Data (LV 2)	
		at 6 rpm	700
30		at 60 rpm	500

25

## 5.

35		<u>ingredient</u>	<u>parts by weight</u>
		Epotuf™ 3020 25TPGDA	10
	30	Uretuf™ 4210	40
		Trimethylolpropane triacrylate	20
40		Isobornyl acrylate	34.5
		Irgacure™ 184	0.5
		Aerosil™ 200	1.0

35

		Viscosity Data (LV 3)	
45		at 6 rpm	2120
		at 60 rpm	1034

		Thixotropic Index	2.05
--	--	-------------------	------

40

50

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## 6.

<u>ingredient</u>	<u>parts by weight</u>
Epotuf™ 3020 25TPGDA	20
Uretuf™ 4210	30
Trimethylolpropane triacrylate	20
Isobornyl acrylate	29.5
Irgacure™ 184	0.5
Aerosil™ 200	1.0
Viscosity Data (LV 3)	
at 6 rpm	2840
at 60 rpm	1290
Thixotropic Index	2.2

## 7.

<u>ingredient</u>	<u>parts by weight</u>
Epotuf™ 3020 25TPGDA	15
Uretuf™ 4210	30
Trimethylolpropane triacrylate	20
Isobornyl acrylate	33.5
Irgacure™ 184	0.5
Aerosil™ 200	1.0
Viscosity Data (LV 3)	
at 6 rpm	1360
at 60 rpm	888
Thixotropic Index	2.4

The 6 and 7 compositions were UV cured under the following conditions. Two lamps were employed at 400 Watts/inch each using medium pressure mercury lamps at 21-23 feet per minute. The following doses and intensities corresponding to the denoted spectral bands were employed.

## 35

<u>Spectral Bands</u>	<u>Doses (mJ/cm<sup>2</sup>)</u>	<u>Intensity (mW/cm<sup>2</sup>)</u>
A	683	275
B	588	228
C	85	35
V	372	150

Additionally, "31211" represents an unsaturated isophthalic acid-based polyester commonly used in making finished gel coats for the cultured marble industry. "N-35" represents a more concentrated form of "U-3039".

Exposed and unexposed results are set forth in Table 2.

Table 2

	1	2	3	4	5	6	7	8	9
Filler									
1	100								
2		100							
3			100	100					
4					100				
5						100	100	100	
6									100
31211									
Isophthalic acid									
N-35	0.3	0.3			0.3	0.3			
Thickness	10 mils	10	10	10	10	10	10	10	20
Lamp test	~10	~10	4	9	~10	~10	9	4	NA
Marble-like	0.75	75	75	75	75	75	75	75	
Marble									75
Unexposed									
1	75.71	75.47	76.07	76.32	75.9	75.61	76.14	76.35	72.16
2	-1.33	-1.33	-1.33	-1.29	-1.22	-1.32	-1.37	-1.32	-0.8
3	4.05	3.86	4.08	4.24	3.75	3.56	4.1	4.17	4.61
Exposed									
1	74.57	74.56			74.85				71.89
2	-1.57	-1.6			-1.67				-0.7
3	7.78	7.38			7.9				6.11
Exchanges	3.73	3.52			4.15				1.5

Table 2 (cont'd)

	10	11	12	13	14	15	16	17	18	19
File										
5										
6										
7										
8			100	100						
9					100	100				
10							100	100		
11									100	100
12										
13	100	100								
14	0.5	0.5								
15										
16	10	20	7	10	7	10	7	10	10	20
17										
18	-10	-10	-10	-10	-10	-10	-10	-10	-10	-10
19										
20										
21	75	75	75	75	75	75	75	75	75	
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Example 5**Stain Resistance Study**

Films and marble castings are prepared in accordance with Example 3. Stain testing is performed by a physical testing team at Reichhold, Inc. in Durham, North Carolina following ANSI Z-124.3 and Z-124.6 standard procedures.

Table 3

Composition No.		10		11	
Stain Resistance Test, ANSI Z-124.3		COV	UNC	COV	UNC
1	Black crayon	1	1	2	2
2	Black liquid shoe polish	2	2	2	2
3	Blue washable ink	2	2	2	2
4	Gentian violet solution	2	2	2	2
5	Red lipstick	1	1	1	1
6	Hair dye (brown)	1	1	1	1
7	Iodine Solution	5	5	3	5
Total		14	14	13	15
Overall Total (Max = 50)		28		28	

Composition No.		10		11	
Stain Resistance Test, ANSI Z-124.6		COV	UNC	COV	UNC
1	Black crayon	1	1	2	2
2	Black liquid shoe polish	2	2	2	2
3	Blue washable ink	2	2	2	2
4	Gentian violet solution	2	2	2	2
5	Red lipstick	1	1	1	1
6	Hair dye (brown)	1	1	1	1
7	Mercurochrome solution, 2%	1	1	1	1
8	Beet juice	1	1	1	1
9	Grape juice	1	1	1	1
10	Wet tea bag	1	1	1	1
Total		13	13	14	14
Overall Total (Max = 64)		26		28	

The gel coat composition 10 refers to the composition set forth in Example 1. The gel coat composition (referred to 11 herein) is in the form of a conventional unsaturated polyester. The column "COV" refers to the sample containing a gel coat composition and designated contaminant thereon being covered, while the "UNC" column refers to uncovered samples. Lower numbers in the table denote more favorable results. As shown, the gel

coat compositions of the invention display excellent results relative to a conventional coat composition.

#### Example 6

##### **Stain Resistance Study**

The procedure according to Example 5 was repeated except that the gel coat composition included 39.5 percent by weight of isobornyl acrylate and Aerosil 200 was omitted (see composition 4). As shown in Table 4, the composition displays largely favorable results when exposed to a number of staining materials. "NO" refers to the samples being covered and "YES" refers to the samples being uncovered.

#### Example 7

##### **Stain Resistance Study**

The procedure according to Example 6 was repeated except that the following gel coat composition was employed (see 7):

<u>Ingredient</u>	<u>parts per hundred</u>
Epotuf™ 3025 25TPGDA	15
Uretuf™ 4210	30
Trimethylolpropane triacrylate	20
isobornyl acrylate	33.5
Irgacure 184	0.5
Aerosil 200	1.0

Stain resistance results are set forth in Table 4. As shown, the composition displays largely favorable results when exposed to a number of staining materials.

Table 4  
STAIN RESISTANCE ANSI 124.6 Method.

Composition No.	4		7	
	NO	YES	NO	YES
1) BLACK CRAYON	1	1	1	1
2) BLACK LIQUID SHOE POLISH	1	1	1	1
3) BLUE WASHABLE INK	1	1	1	1
4) GENTIAN VIOLET 2% SOLUTION	1	1	1	1
5) RED LIPSTICK	1	1	1	1
6) BROWN HAIR DYE	1	1	1	1
7) MERCUROCHROME 1% Solution	1	1	1	1
8) BEET JUICE	1	1	1	1
9) GRAPE JUICE	1	1	1	1
10) WET TEA BAG	1	1	1	1
Sub-totals	10	10	10	10
Totals	20		20	

Max. Rating = 64.

### Example 8

#### Point Impact Resistance Study

Various films and marble castings are produced as described herein. Panels are then tested for impact strength using a Gardner Impact Tester with a 4-lb. weight and a rounded steel hammer. Single readings are taken at ever increasing heights until which time a matrix crack (in the marble) occurs or a crack could be observed in the film around the perimeter of the impact crater. The testing continues until which duplicate failures are measured. This height is recorded as the point of failure.

Table 5 illustrated the results of the impact resistance study. As shown, the films and marble castings employing the gel coats of the invention display good results.



Table 5

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	100													
2		100												
3			100	100										
4					100	100								
5							100	100	100					
6										100	100			
7												100	100	
8														100
9														
10	10	10	10	10	7	10	7	10	20	7	10	10	10	20
11	RTP	RTP	Fusion	Fusion	RTP	RTP	RTP	RTP	RTP	RTP	RTP	Fusion	Fusion	RTP
12	-10in.	-10	4in	9in	-10	-10	-10	-10	-10	-10	-10	4	9	N/A
13	36in	>36	20	24	>36	>36	>36	>36	35	27	27	10	24	13
14	144	>144	80	96	>144	>144	>144	>144	140	108	108	40	96	52
15	Matrix	Non e	Matrix	Matrix	Non e	Non e	Non e	Non e	Film	Matrix	Matrix	Film	Film	Film

Note: Nominal film thickness. Actual values were later measured to be ~  
 1/2 of values shown.

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The present invention has been described in detail above. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein above; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art.

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**Claims**

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**THAT WHICH IS CLAIMED:**

1. A gel coat composition comprising:  
from about 5 to about 95 percent by weight of a resinous or oligomeric  
component containing (meth)acrylate functionality;  
from about 5 to about 95 percent by weight of a (meth)acrylate ester;  
and  
from about 0.2 to about 10 percent by weight of a polymerization  
initiator that can be activated under ultraviolet light.

2. The gel coat composition according to Claim 1, wherein said  
resinous or oligomeric component containing (meth)acrylate functionality is a  
urethane (meth)acrylate.

3. The gel coat composition according to Claim 1, wherein said  
resinous or oligomeric component containing (meth)acrylate functionality is an  
epoxy (meth)acrylate.

4. The gel coat composition according to Claim 1, wherein said  
(meth)acrylate ester is selected from the group consisting of  
tetrahydrofurfuryl(meth)acrylate, 2-ethylhexyl(meth)acrylate, methoxyethyl  
(meth)acrylate, N-vinylpyrrolidone, phenyl(meth)acrylate, 2-hydroxyethyl  
(meth)acrylate, diethyleneglycol di(meth)acrylate, tetraoxyethyleneglycol  
di(meth)acrylate, trimethylolpropane tri(meth)acrylate, dipentaerythritol  
hexa(meth)acrylate, trimethylolpropane di(meth)acrylate, tripropyleneglycol  
di(meth)acrylate, isobornyl (meth)acrylate, pentaerythritol tetra(meth)acrylate,  
and mixtures thereof.

5. The gel coat composition according to Claim 1, wherein said  
polymerization initiator is selected from the group consisting of carbonyl  
compounds, xanthone compounds, and sulfur compounds.

6. The gel coat composition according to Claim 1, further  
comprising a performance additive selected from the group consisting of  
organic thixotropes, inorganic thixotropes, organic pigments, inorganic

5 pigments, stabilizers, defoaming agents, wetting agents, leveling agents, and combinations thereof.

7. A gel coat composition comprising:

10 5 a resinous or oligomeric component containing (meth)acrylate functionality;

a (meth)acrylate ester;

15 a polymerization initiator that can be activated under ultraviolet light, said polymerization initiator being a non-peroxide initiator;

10 wherein said gel coat composition is devoid of aryl vinyl monomer.

20 8. The gel coat composition according to Claim 7, wherein said resinous or oligomeric component containing (meth)acrylate functionality is a urethane (meth)acrylate.

25 9. The gel coat composition according to Claim 7, wherein said resinous or oligomeric component containing (meth)acrylate functionality is an epoxy (meth)acrylate.

30 20 10. The gel coat composition according to Claim 7, wherein said (meth)acrylate ester is selected from the group consisting of tetrahydrofurfuryl(meth)acrylate, 2-ethylhexyl(meth)acrylate, methoxyethyl (meth)acrylate, N-vinylpyrrolidone, phenyl(meth)acrylate, 2-hydroxyethyl (meth)acrylate, diethyleneglycol di(meth)acrylate, tetraoxyethyleneglycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, dipentaerythritol 25 hexa(meth)acrylate, trimethylolpropane di(meth)acrylate, tripropyleneglycol di(meth)acrylate, isobornyl (meth)acrylate, pentaerythritol tetra(meth)acrylate, and mixtures thereof.

45 30 11. The gel coat composition according to Claim 7, wherein said polymerization initiator is selected from the group consisting of carbonyl 50 compounds, xanthone compounds, and sulfur compounds.

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12. The gel coat composition according to Claim 7, further comprising a performance additive selected from the group consisting of organic thixotropes, inorganic thixotropes, organic pigments, inorganic pigments, stabilizers, defoaming agents, wetting agents, leveling agents, and mixtures thereof.

13. An article of manufacture comprising:  
a substrate having a surface;  
a gel coat composition present on the surface of the substrate, the gel coat composition comprising a resinous or oligomeric component containing (meth)acrylate functionality; a (meth)acrylate ester; and a polymerization initiator that can be activated under ultraviolet light, the polymerization initiator being a non-peroxide initiator; and wherein said gel coat composition is devoid of aryl vinyl monomer.

14. The article of manufacture according to Claim 13, wherein said substrate is selected from the group consisting of a reinforced plastic based on a thermosetting resin, fillers, and combinations thereof.

15. The article of manufacture according to Claim 14, wherein the thermosetting resin is selected from the group consisting of an unsaturated polyester resin, a vinyl ester resin, an epoxy resin, an acrylic resin, and a urethane resin.

16. The article of manufacture according to Claim 14, wherein the fillers are selected from the group consisting of fiberglass, carbon fiber, naturally occurring fibrous compound, calcium carbonate, aluminum trihydrate, talc, ground silicates, silica spheres, polymeric spheres, pigmented particulates, and combinations thereof.

17. The article of manufacture according to Claim 13, wherein the resinous or oligomeric component containing (meth)acrylate functionality is a urethane (meth)acrylate.

5                   18. The article of manufacture according to Claim 13, wherein the  
resinous or oligomeric component containing (meth)acrylate functionality is an  
epoxy (meth)acrylate.

10                   5                   19. The article of manufacture according to Claim 13, wherein the  
(meth)acrylate ester is selected from the group consisting of  
15                   tetrahydrofurfuryl(meth)acrylate, 2-ethylhexyl(meth)acrylate, methoxyethyl  
(meth)acrylate, N-vinylpyrrolidone, phenyl(meth)acrylate, 2-hydroxyethyl  
20                   10                   (meth)acrylate, diethyleneglycol di(meth)acrylate, tetraoxyethyleneglycol  
di(meth)acrylate, trimethylolpropane tri(meth)acrylate, dipentaerythritol  
25                   15                   hexa(meth)acrylate, trimethylolpropane di(meth)acrylate, tripropyleneglycol  
di(meth)acrylate, isobornyl (meth)acrylate, pentaerythritol tetra(meth)acrylate,  
and mixtures thereof.

25                   20                   20. The article of manufacture according to Claim 13, wherein the  
polymerization initiator is selected from the group consisting of carbonyl  
30                   20                   compounds, xanthone compounds, and sulfur compounds.

35                   25                   21. The article of manufacture according to Claim 13, further  
comprising a performance additive selected from the group consisting of  
organic thixotropes, inorganic thixotropes, organic pigments, inorganic  
40                   25                   pigments, stabilizers, defoaming agents, leveling agents, wetting agents, and  
mixtures thereof.

45                   30                   22. A method of forming an article of manufacture comprising:  
applying a gel coat composition to a surface of a mold, the gel coat  
composition comprising a resinous or oligomeric component containing  
45                   30                   (meth)acrylate functionality; a (meth)acrylate ester; and a polymerization  
initiator that can be activated under ultraviolet light;  
curing the gel coat composition;  
50                   50                   lining the cured gel coat composition with a substrate to form an  
assembly; and

de-molding the assembly to form an article of manufacture.

23. The method according to Claim 22, wherein said applying step comprises spraying or brushing the gel coat composition to the surface of the mold.

24. The method according to Claim 22, wherein the substrate is selected from the group consisting of a reinforced plastic based on a thermosetting resin, fillers, and combinations thereof.

25. The method according to Claim 24, wherein the thermosetting resin is selected from the group consisting of an unsaturated polyester resin, a vinyl ester resin, an epoxy resin, an acrylic resin, and a urethane resin.

26. The method according to Claim 24, wherein the fillers are selected from the group consisting of fiberglass, carbon fiber, naturally occurring fibrous compound, calcium carbonate, aluminum trihydrate, talc, ground silicates, silica spheres, polymeric spheres, pigmented particulates, and combinations thereof.

27. The method according to Claim 22, wherein the resinous or oligomeric component containing (meth)acrylate functionality is a urethane (meth)acrylate.

28. The method according to Claim 22, wherein the resinous or oligomeric component containing (meth)acrylate functionality is an epoxy (meth)acrylate.

29. The method according to Claim 22, wherein the (meth)acrylate ester is selected from the group consisting of tetrahydrofurfuryl(meth)acrylate, 2-ethylhexyl(meth)acrylate, methoxyethyl (meth)acrylate, N-vinylpyrrolidone, phenyl(meth)acrylate, 2-hydroxyethyl (meth)acrylate, diethyleneglycol di(meth)acrylate, tetraoxyethyleneglycol



5 di(meth)acrylate, trimethylolpropane tri(meth)acrylate, dipentaerythritol  
hexa(meth)acrylate, trimethylolpropane di(meth)acrylate, tripropyleneglycol  
di(meth)acrylate, isobornyl (meth)acrylate, pentaerythritol tetra(meth)acrylate,  
10 and mixtures thereof.

5  
30 The method according to Claim 22, wherein the  
polymerization initiator is selected from the group consisting of carbonyl  
15 compounds, xanthone compounds, and sulfur compounds.

10  
31. The method according to Claim 22, wherein the gel coat  
composition further comprising a performance additive selected from the  
20 group consisting of organic thixotropes, inorganic thixotropes, organic  
pigments, inorganic pigments, stabilizers, wetting agents, defoaming agents,  
leveling agents, and mixtures thereof.

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 99/22596

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09D4/06 C08F290/14 C09D4/00 C08F220/12 C08F222/10  
B29C37/00 B29C70/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09D C09J C08F B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X,P	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 04, 30 April 1999 (1999-04-30) & JP 11 021325 A (HITACHI CHEM. CO. LTD.), 26 January 1999 (1999-01-26) abstract see also Derwent abstract n° 1999-163237 and Chemical Abstracts 130:169282 --- -/-	1-3, 5, 7, 8, 10, 11, 13-17, 19, 20

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"A" document member of the same patent family

Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/22596

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 91, no. 30, 5 June 1985 (1985-06-05) & JP 60 015441 A (TOYOJI TSUCHIHARA), 26 January 1985 (1985-01-26) abstract see also Derwent abstract n° 1985-058982	1-5, 7-11, 13, 15, 17-20
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X	EP 0 214 930 A (CIBA GEIGY AG) 18 March 1987 (1987-03-18)  page 2, line 9 - line 65 page 5, line 15 - line 21 page 5, line 62 - page 6, line 15 page 6, line 49 - line 64 example 1 claims 1, 4, 6, 10, 14	13-16, 18-26, 28-31
Y	idem.	1-31
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Information on patent family members

Int. Application No

PCT/US 99/22596

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